



## A review of large-scale fire testing focusing on the fire behaviour of chemicals,

Guy Marlair, Claude Cwiklinski, Fabrice Marliere, Hervé Breulet, Christian Costa

### ► To cite this version:

Guy Marlair, Claude Cwiklinski, Fabrice Marliere, Hervé Breulet, Christian Costa. A review of large-scale fire testing focusing on the fire behaviour of chemicals,. Interflam 96, Mar 1996, Cambridge, United Kingdom. pp.371-382. ineris-00971959

**HAL Id: ineris-00971959**

**<https://hal-ineris.archives-ouvertes.fr/ineris-00971959>**

Submitted on 3 Apr 2014

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## A REVIEW OF LARGE-SCALE FIRE TESTING FOCUSING ON THE FIRE BEHAVIOUR OF CHEMICALS

Guy Marlair, Claude Cwiklinski, Fabrice Marlière, Institut de l'Environnement Industriel et des Risques (INERIS), FRANCE,  
H. Breulet, ISSeP, BELGIUM,  
C Costa, Rhône-Poulenc Industrialisation, FRANCE

### ABSTRACT

A review is presented of the main features of the fire behaviour of chemicals, as assessed by large-scale experiments in a semi-confined environment. The paper focuses on those chemicals which contain at least one hetero-atom fixed to their hydrocarbon basic structure, rather than on classical hydrocarbons for which much work has already been published.

It emphasises results dealing more especially with the generation of heat and toxic combustion products in well ventilated conditions. Some aspects of the implication of lab-scale tests in the related area are also proposed, for comparison purposes. Finally, comments in terms of progress in the risk assessment of thermal and chemical impacts of fires of chemicals are finally made in matter of a conclusion.

### INTRODUCTION

An extensive and urgent need of useful engineering data dealing with the fire hazard of chemicals was recognised in Europe in the mid 70's. This concern has increased even more in the 80's with the implementation of reinforced legislation in the field of industrial risks -enhanced by the so-called "Seveso Directive" 82/501/EEC and its amendments<sup>1</sup> and because some real case accidents have affected the Environment dramatically<sup>2,3</sup>.

INERIS and few other European centres contributed to the subsequent applied research by the use of large-scale fire testing techniques, which were thought able to bring macroscopic, significant and meaningful results of direct practical use for the industry.

Within this overall context, the present paper is reporting mainly on fire knowledge achieved experimentally, at a large scale, on a variety of chemicals, mostly at the INERIS large scale fire testing facility located in Verneuil-en-Halatte, France.

In the field, INERIS has gained considerable experience on a variety of products acquired over a long term period of time (nearly ten years). Most tests were carried out in ventilated conditions in accordance with ISO TR 9122 fire classification<sup>4</sup>, since such conditions were typical of French industrial premises.

Chemicals investigated thus far have been most of the time commercially-important materials such as pesticides (diuron, dimethoate, high sulfur content fungicides, other insecticides and herbicides ...), fertilizers (ternary type), pharmaceuticals, nitrogenated solvents and other liquid basic chemicals (acetonitrile, adiponitrile, ethylene diamine, aromatic isocyanates TDI and PMDI). C-H or C-H-O solvents (n-Heptane, isooctane, toluene, méthanol) have also been tested as reference materials.

## TOOLS FOR LARGE SCALE TESTING OF CHEMICALS AND INDUSTRIAL PRODUCTS

Early testing facilities consisted of free open sites where very simple but useful series of large scale burn tests were carried out in freely ventilated conditions on classical hydrocarbons, only requiring pans of various sizes in terms of special equipments. Major results achieved from such types of experiments (largely discontinued today by scientists for environmental reasons with few exceptions<sup>5</sup>) were a first and still partially valid evaluation of scale effects of fires on flame height and regression rate of liquid pools for numerous products. A well known example of experimental work achieved that way was the pioneering experimental study of Blinov and Khudyakov<sup>6</sup>. Review papers on pool burning with hydrocarbon fuels were made available in the early 70's<sup>7</sup> and updated in the 80's<sup>8,9</sup>.

A further step was accomplished with the appearance of experimental test rigs which allowed large-scale testing of rooms fully equipped with furniture as in private dwellings. For the industrial needs, two types of large scale versatile units were then developed, more or less in a parallel way, and both are still in use. The first design consists of a large hall fitted with a hood system suitable for collecting and characterising all the fire gases resulting from in-door storage commodity burn tests, rating up to about 10 MW of effective heat release. This concept was first developed by Factory Mutual (USA), the Swedish laboratory SP recently commissioned the same kind of equipment in Borås<sup>10</sup>. Those equipments and related procedures are adequately designed for the measurements of the actual heat release rates of fires.

The other type of equipment developed for large scale fire testing is the wind tunnel design to which the INERIS main fire testing facility belongs. Formerly designed for studying the fire risk in coal mines, some of the existing equipment has extended its scope to fires in road and rail traffic tunnels and inside warehouses and other industrial storage premises.

Figure 1 shows a perspective view of the equipment used for most experiments reviewed in this paper, outlining its main dimensions.

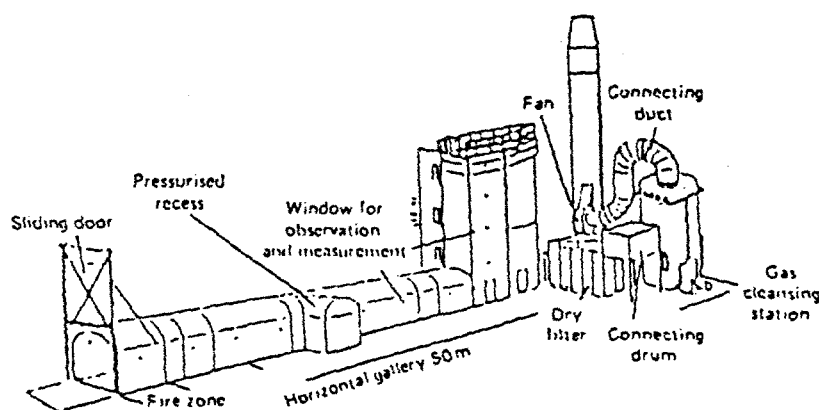


Figure 1 : view of the INERIS fire test gallery

Basic information was reported<sup>11,12</sup> together with some example results on fire tests involving solid and liquid chemicals. From the air admittance (controlled by a sliding door) to the stack diluting the fire gases, the unit is composed of :

- a horizontal section (the wind tunnel part) which is nearly 50 m long and presents an open section of about 10 m<sup>2</sup>,

- a vertical "tower", about 12 m high, with a rectangular cross section (6 m<sup>2</sup>), at the top of which the main sampling ports are positioned for the analysis of the fire gases and the heat release rate measurements (at a place so-called the "mixing point"),
- a vertical column guiding the fluids (the fire gases mixed with entrained air) to the gas cleaning unit which may also serve as a cooling unit (use of inner water curtains),
- a gas cleaning unit comprising a dry dust filter and a wet scrubber,
- the final attachments (exhaust fan and stack).

The overall volume of the unit is about 600 m<sup>3</sup>, to which an 18 m<sup>3</sup> enclosure must be added which may be used with or without connexion with the main unit, depending on the aims of experiments. The walls comprise an external metal sheet of 5 mm and inner linings made of both insulation and refractory materials.

Testing procedures generally applied in the fire gallery are designed to keep environmental parameters as far as possible representative of the real fire scenario studied. They must be able to meet many goals in a single run, due to their costs. Therefore, related fire tests are systematically and heavily instrumented with local and distant measurements allowing thermal and mass balance assessments to analyse efficiently the chemical as well as the thermal responses of the fires, following some of Peacock's suggestions<sup>13</sup>. A video recording of the fires is also considered of the greatest importance, as visual observation may play a major role in the understanding of important phenomena related to the experimental fires, as recently outlined by Hirano and Saito<sup>13bis</sup>. More specific aims depending on each work undertaken may apply for specific set-up and testing protocols (testing liquified gases in a pool configuration for instance).

From a general point of view, an adequate test procedure for characterising the fire behaviour of solid materials on a large-scale is a rather complex goal as it must take into account that the combustion rate as well as main properties of the fire plume resulting from a fire scenario closely depend on :

- the chemical nature and formulation of the product,
- the state of division of the commercial product (basically due to the actual chemical physical state and at a macroscale, consequent upon the packaging, conditioning, and storage conditions as well),
- the confinement of the storage premises
- a three dimensional character.

For testing the fire hazard of generic liquids to assess the fire behaviour of bulk storage capacities , the pool fire configuration chosen and continuously improved by INERIS is based upon the technical approach of Emori and Saito<sup>14</sup>

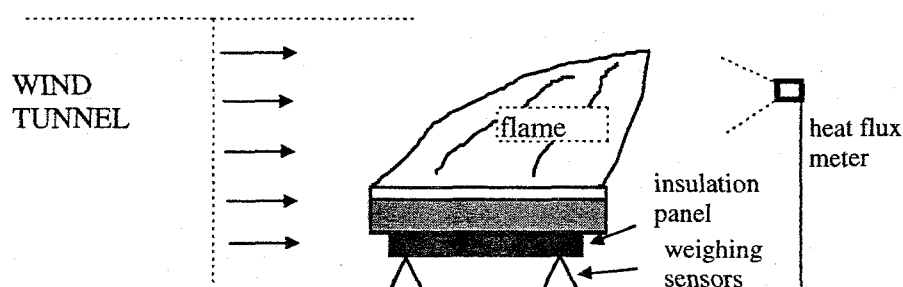


Figure 2 : experimental principle for ventilated pool fires

According to this experimental arrangement, the pan determining the size of the burning pool of the tested product is installed in a wind tunnel (see figure 2) and is lying on a weighing platform. Optional features deal with the possibility of providing a burning phase with the level of product being maintained constant in order to observe a steady state. More simply the product may be burnt in a batch procedure where a determined amount of product is totally poured in the pan prior to the ignition. The constant level facility is fairly easily obtained for most fuels by providing a simple regulation loop which includes a thermocouple sensor measuring the temperature at the desired position of the interface between the liquid and vapour phase. Both techniques are useful depending on the fire scenario which is to be addressed. A constant level test, for example, is related to a pool fire being fed in fuel continuously from a leakage in a damaged storage capacity, whilst the alternative procedure represents a pool fire scenario inside a capacity containing a combustible liquid.

The experience of INERIS in the field considerably increased and was validated further through the EUREKA499 "Firefun" project, where pool fires of heptane from 1m<sup>2</sup> to 3 m<sup>2</sup> with a constant level mode were monitored from a distance of more than 350 m from the pan<sup>15</sup>.

### SOME RESULTS DEALING WITH THE THERMAL AND CHEMICAL ASPECTS OF FIRES INVOLVING PESTICIDES AND OTHER ATYPIC CHEMICALS

Dealing with the fire problem with pesticides, we comment hereafter on the chemical issue of such types of fires, based on a series of 5 different large scale (150 kg to 400 kg) experiments carried out in our fire gallery. Detailed information on procedures and overall results may be found in another paper regarding diuron and dimethoate<sup>16</sup>. All products were tested as commercial formulations including the active chemical, the additives (inert or combustible) and the packaging materials as well. Three of the products are named with a code due to commercial agreements. "Product A" refers to a test involving a single product, "pallet B" refers to a "cocktail" commodity of 5 different commercial grade herbicides, "pallet C" refers to a test involving 5 different herbicides in a procedure very similar to "pallet B". Additional information refers to the hetero-atoms existing in the formulations involved.

Table 1 gives the fate of those chemicals in fire conditions in terms of emissions of toxic combustion products.

	diuron (a) C <sub>9</sub> H <sub>10</sub> N <sub>2</sub> OCl <sub>2</sub>	dimethoate (b) C <sub>5</sub> H <sub>12</sub> NO <sub>3</sub> PS <sub>2</sub>	product A C, H, O, N	pallet B C, H, N, O, S, Cl	pallet C C, H, N, O, S, Cl
NO <sub>x</sub>	6.4	1.0	8.2	23	1.7
HCN	5.5	7.1	0.4	3.6	1.2
MIC	(c)	traces	0.2	(c)	(c)
amines	traces	(d)	4.9	0.1	traces
SO <sub>2</sub>	-	31.3	-	81	74
CH <sub>3</sub> SH	-	20.9	-	(d)	(d)
HCl	50.8		-	23	31

survival fractions of pesticides	no	yes	no	yes	no
--	----	-----	----	-----	----

(a) product used for the test was 80% of diuron diluted in inert materials

(b) tested as a mixture of 400 g/l in organic solvents (mainly xylene)

(c) not detected ; (d) not available

Table 1 : yields of gaseous toxic emissions (in % of theoretical maximum) from large-scale fire tests involving various pesticides

In all cases, the tested commodity comprised a wood pallet with packaging materials made of cardboard and polyethylene. In all experiments, solid residues were observed. Survival fractions of active chemicals from the pesticide formulations were sometimes noticed as reported by Atkinson et al with organophosphorous compounds<sup>17</sup> in those experiments where very turbulent flaming burning phases were reached.

From table 1, we may point out the great variation in the conversion ratio of the hetero-atoms in the toxic gaseous components.

Large-scale testing is clearly sometimes the only way to qualify very specific fires such as those involving mineral products e.g. fertilizers, sulfur... which are commercially important chemicals containing no combustible carbon in their chemical structure.

Ternary fertilizer represents a specific hazard related to behaviour in fire conditions. Although it is excessive to speak of the fire hazard with such an essentially mineral material, a highly exothermic thermal decomposition may be feared. In bulk storages, this can give rise to thermal threats as with more classical fires.

The thermal and chemical aspects of such a fire have been examined experimentally at INERIS, as a consequence of an actual French accident involving 850 tons of 15-8-22 NPK fertilizer in bulk storage near the town of Nantes. The procedure adopted was a simulated bulk storage of 1 ton capacity containing a similar fertilizer inside the fire gallery. Decomposition was very successfully initiated by a electrical plate raised to only 220°C. Important results regarding the thermal aspect were (I) a much higher thermal decomposition propagation rate than expected (From the classical medium scale test carried out by the manufacturers to qualify the reactivity of such products), (II) a rather small thermal heat release and (III) the refractory property of the solid residues. Relevant fire-fighting techniques must take care of solid phase transformations occurring in the residues to cool the burning storage with some efficiency. The major chemical findings of the large scale test carried out were that half of the product is to be expected to be released as a mixture of toxic chlorinated and nitrogenated compounds in significant amounts (HCl, Cl<sub>2</sub>, N<sub>2</sub>O, NO<sub>2</sub>, HNO<sub>3</sub>, ) diluted in water vapour, ammonium chloride and molecular nitrogen. More exhaustive information related to this test was reported previously by Cwiklinski<sup>18</sup>.

Sulfur fires were also briefly investigated in the form of high sulfur content (80% to 99%) in fungicide trade products. Tests were carried out on two quality product (a technically pure grade of micronised sulfur powder and an 80% S containing grade diluted with 20% of inert material). They revealed, surprisingly, completely different fire behaviours. The pure grade type of sulfur turned rapidly into a moderately active blue flaming pool fire, with a small burning velocity (some 4 to 8 g m<sup>-2</sup> s<sup>-1</sup>) which was expected since the melting point of sulfur is about 112°C. The 80% grade on the other hand was looking like a non flaming coal dust fire leaving a great part of solid residue, but released as well massive amounts of SO<sub>2</sub>, with practically no visible fire activity. In the latter case, a non glowing solid layer forms at the pool surface and may induce a false impression of natural extinction.

## **FIRES INVOLVING NITROGENATED SOLVENTS AND AROMATIC ISOCYANATES**

Very few experiments have been reported previously on the fire behaviour of liquid nitrogenated solvents, even on the lab scale. We have just noticed the earlier work of Burgess<sup>19</sup> who included in their list of investigated products UDMH (unsymmetrical dimethyl hydrazine) and DETA (diethylene triamine) in terms of burning rates, and more recently, the contribution of Bartelds and coworkers<sup>20</sup> who have also carried out experiments at a medium scale including EDA (ethylene diamine) and TDI (toluene diisocyanate) alone or in a mixture with xylene<sup>20</sup> with the aim of evaluating emissions.

INERIS has been studying the fire behaviour of liquid nitrogenated products within several long term applied research programmes including products like TDI, "ACN"(acetonitrile) or ADN

# MISTRAL 2

adiponitrile pool fire (1 m<sup>2</sup>)

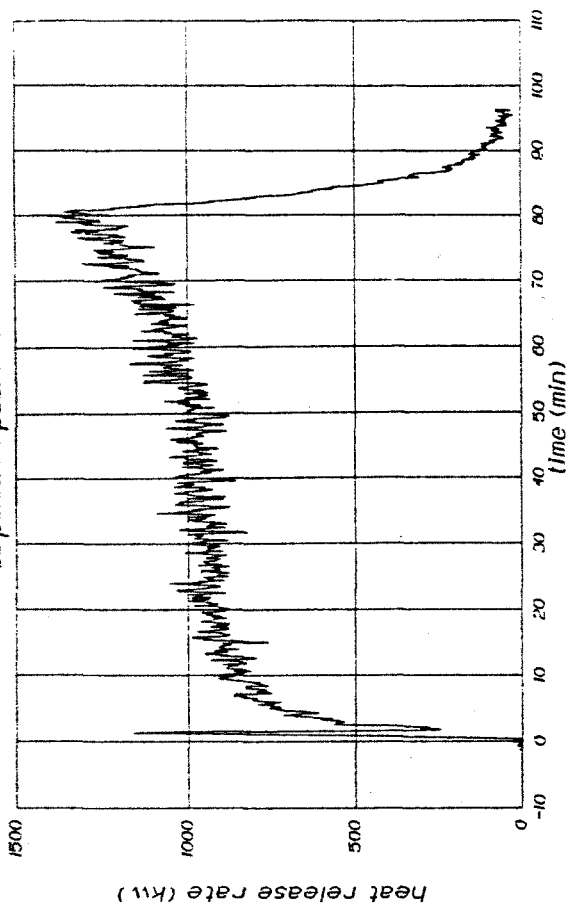


Figure 4 : HRR curve of a 1 m<sup>2</sup> pool fire of ADN

# MISTRAL 2

NOx concentrations in fire gases of pool fires

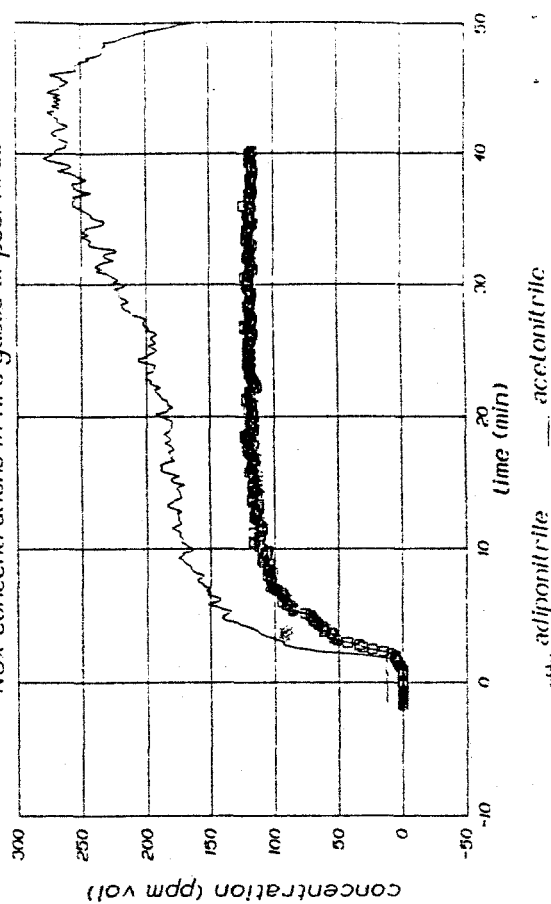


Figure 6 : Example of NO<sub>x</sub> concentrations in well ventilated pool fires

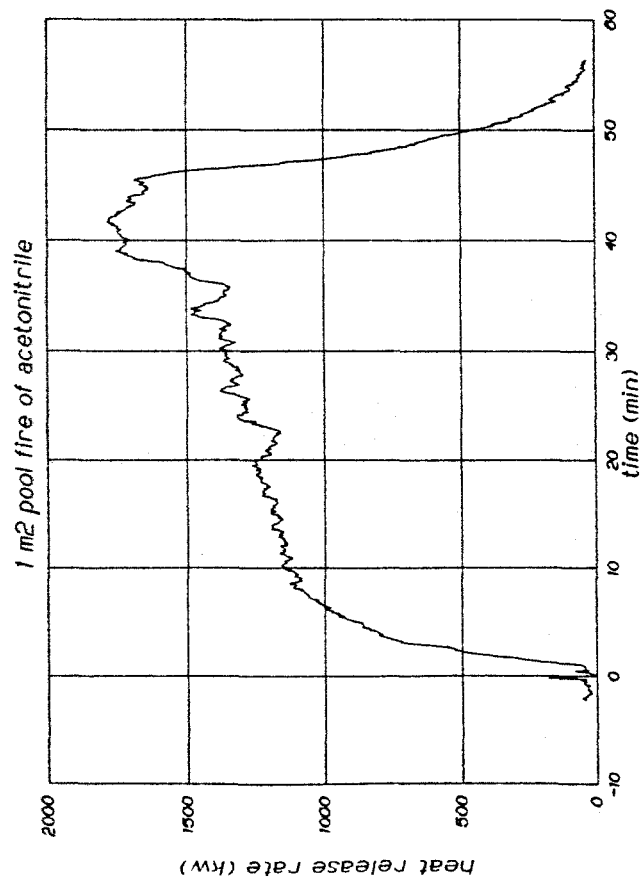


Figure 3 : HRR curve of a 1 m<sup>2</sup> pool fire of Acetonitrile

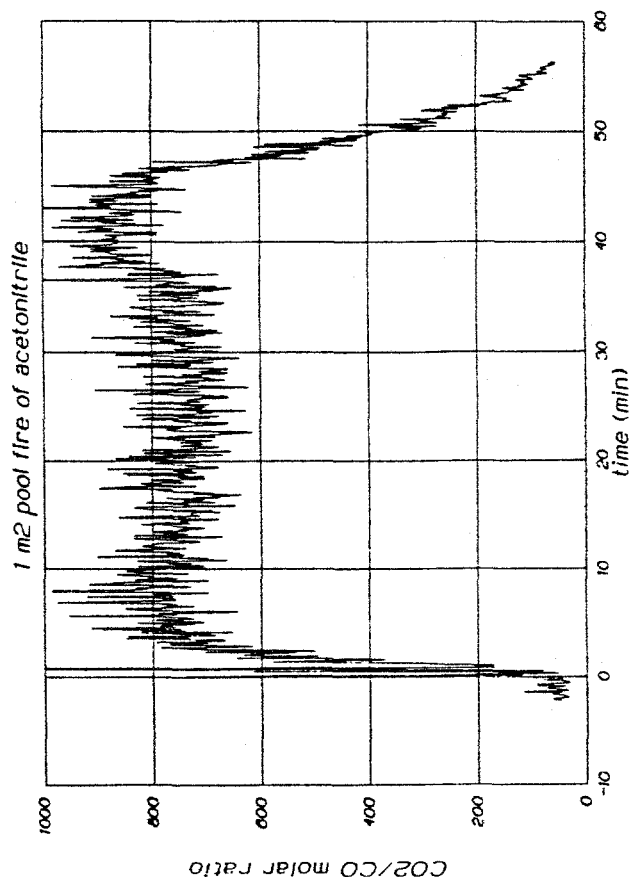


Figure 5 : CO<sub>2</sub>/CO molar ratio (ACN pool fire)

(adiponitrile). Quantities of products involved range between 20 to more than 300 liters depending on scale and expected test duration (at least 40 min)

Table 2 summarizes the physico-chemical properties of the whole set of products containing nitrogen which were involved in the experiments plus some additional basic thermochemical data. As shown, nitrogen-fuel is present in various types of functional groups in the chemical structures involved. Nitrogen appears in nitrile groups in ACN and ADN, or in isocyanate groups in TDI and PMDI, or linked in the form of amine groups in EDA.

name of products	formulae	mol. weight (g)	N content (%)	Boil. Point (°C)	Freez. Point (°C)	Flash Point (°C)	density (a) (g/cm <sup>3</sup> )	$\Delta H_{\text{comb}}$ (kJ/g)	$\Delta h_{\text{vap}}$ (kJ/g)
ACN	C <sub>2</sub> H <sub>3</sub> N	41	34.1	82	- 45	+6	0.79	30.1	0.73
ADN	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub>	108	25.9	295	+ 2.4	+ 163	0.96	33.1	0.56
TDI	C <sub>9</sub> H <sub>6</sub> O <sub>2</sub> N <sub>2</sub>	174	16.1	251	< 15	130	1.22	23.6	-
PMDI (b)	C <sub>15</sub> H <sub>10</sub> O <sub>2</sub> N <sub>2</sub> (e)	320/400	11/11.2	-	< 10	230 (e)	(1.20)	n.a.	n.a.
EDA	C <sub>2</sub> H <sub>8</sub> N <sub>2</sub>	60	46.6	116	+8.5	+ 40	0.909	28.6	0.67
DETA (c)	C <sub>4</sub> H <sub>13</sub> N <sub>3</sub>	103	40.8	207	- 39	+ 98	0.95	30.9	n.a.
UDMH (c)	C <sub>2</sub> H <sub>8</sub> N <sub>2</sub>	60	46.6	249	- 58	- 15	0.79	32.9	0.61
Heptane (d)	C <sub>7</sub> H <sub>16</sub>	100	0	98	-90	- 4	0.68	44.6	0.32

(a) at 20°C.

(b) polymeric 4,4' diphenyl methane diisocyanate, see paper<sup>22</sup> for complete information on the structure.

(c) nitrogenated fuels in the work of Burgess<sup>19</sup> only, not tested by INERIS (d) reference hydrocarbon fuel

(e) refers to pure monomeric MDI (C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub>)<sup>22</sup>

**Table 2 : physico-chemical properties and thermochemical data of nitrogenated liquid fuels tested on large (or medium) scale. (Most data from<sup>25</sup> and NFPA325 M).**

The overall phenomenology of diffusive burning features of some of the N-containing fuels tested are graphically illustrated through figures 3 to 6 where examples of directly measured or calculated parameters related to those fires are plotted versus time. Figures 3 and 4 point out how much the heat release rates may be affected by the operational procedure, since a significant increase is systematically observed once the level of liquid is no longer kept constant (terminal phase of most of the runs), due to a modification in the thermal balance at the liquid surface level<sup>21</sup>. The peak value may be about 125 % to 130 % the value reached during the steady state obtained before that procedure change. The first sharp peak in the HRR curve plotted in figure 4 refers to the combustion of the flammable solvent (1 liter of n-heptane) used to make the ignition easier (high flash point of adiponitrile). Figure 5 referring to an acetonitrile pool fire shows the highest CO<sub>2</sub>/CO compared to other products. This parameter has decreased down to 20/50 with aromatic isocyanates pool fires, and was at a mid-range level with adiponitrile (200 to 300).

Finally, figure 6 illustrates the high levels of NO<sub>x</sub> (in terms of volumic concentrations) characterising all products tested. Such a result was naturally expected owing to the relatively high nitrogen content in the molecules (see table 1).

For TDI and ADN, addition of 1 to 2 liters of flammable liquid (heptane) was used before ignition either with a spark alone or through the assistance of a start-up burner to get quick self sustained diffusive and complete burning of the fuels. ACN and EDA, on the other hand, were directly ignited as for flammable liquid hydrocarbons with a simple electrical spark.



PMDI was the only product burning in a quite different manner leaving a large amount of carbonaceous char due to polymerization processes activated by the combustion<sup>22</sup>. No further comment will thus be produced here regarding this product.

Detailed procedures and results regarding 0.25 m<sup>2</sup> and 1 m<sup>2</sup> pool fires of TDI have been also extensively reported by Marlair, Sand and Prager, together with other related work carried out by Bayer and Rhône-Poulenc<sup>23, 24</sup>

	toluene diisocyanate TDI (c)			adiponitrile ADN		acetonitrile ACN		ethylene diamine EDA		
pool area (m <sup>2</sup> )	0.25	1.00	2.00	1.00	2.00	0.66	1.00	0.66	1.00	1.66
burning rate (g.m <sup>-2</sup> .s <sup>-1</sup> ) :	(0.023)	(0.034)	(0.033)	0.029 (0.036)	0.030	0.051 (0.063)	0.050 (0.058)	0.018	0.021	n.s;
T <sub>max</sub> above pool (°C)	700	800	900	850	900	n.a.	900	n.a.	n.a.	n.a.
T <sub>max</sub> under roof (°C)	60	120	240	210	370	> 90	320	150	120	170
T <sub>max</sub> at tower (°C)	35	90	150	115	250	90	170	65	95	125
eff. HRR (kW)	122	560	1250	920	(a)	750	1300	400	(b)	(b)
"conv". HRR (kW)	90	300	480	350	(a)	320	600	(b)	(b)	(b)

(a) not yet available ; (b) not determined ; (c) 1,66 m<sup>2</sup> test : 2 pans of 1 m<sup>2</sup> and 0.66 m<sup>2</sup>

(c) mixture 80/20 of 2,4- and 2,6- isomers.

Figures in parentheses for the burning rates refer to burning phase without a constant level of fuel in the pan. "conv" HRR refers to the gas stream enthalpy as determined at the mixing point in the tower

Table 3 : burning rates and thermal parameters of experimental pool fires

	acetonitrile	adiponitrile	ethylene diamine	TDI
	$\psi_{st}$ (all values in g/g)			
CO <sub>2</sub>	2.15	2.44	1.47	2.28
CO	1.36	1.56	0.93	1.45
NO <sub>x</sub> (as NO <sub>2</sub> )	1.12	0.85	1.53	0.53
HCN	0.66	0.50	0.90	0.31

Table 4 : maximum theoretical yields  $\psi_{st}$  of main combustion products

Table 3 shows a comparison of all nitrogen containing fuels tested in terms of burning rates and thermal response. With the exception of acetonitrile (the lowest molecular weight), all fuels showed a relatively moderate burning rate compared to those of typical flammable liquid hydrocarbons as compiled previously by Babrauskas<sup>9</sup> and in other findings of INERIS related to more classical fuels (n-Heptane : 70 to 90 g m<sup>-2</sup>.s<sup>-1</sup>,...). Those values are also consistent with data quoted by Weiss<sup>25</sup> for other N-fuel compounds like UDMH (asymptotic burning rate equals 51 g.m<sup>-2</sup>.s<sup>-1</sup>) or DETA (asymptotic value equals 22 g.m<sup>-2</sup>.s<sup>-1</sup>). Consequently, the effective heat release rates reveal levels far below the conservative value of 3300 kW /m<sup>2</sup> suggested by Alpert<sup>26</sup> to quickly evaluate the thermal impact of flammable liquid pool fires. These results were indeed more or less expected owing to the relatively high content of N in all the molecules tested (see table 1). Chemical fate of carbon and fuel-N in the gaseous releases is detailed for some experiments in table 5.

Aromatic structures revealed by far the highest levels of CO and soot emissions. With EDA, CO was hardly measurable in some cases. Major yields of N-containing fire gases were NO<sub>x</sub> (85 to 90% of NO) and HCN, whilst other N-containing gases sometimes detected were found in very small amounts in the conditions of the experiments (fuel controlled burning). Global conversion rates of N in total N-containing combustion products were systematically low (in the order of 5% or less) compared to

solid fires (see table 1) which supports the assumption that in this case molecular nitrogen is fortunately (regarding the high potential yields, see table 3) the major N- containing gaseous release.

	EDA	TDI	ACN	ADN
	(all values in mg/g)			
CO	< 1	36	2.4	6
CO <sub>2</sub>	unreliable	1620	2370	2300
No <sub>x</sub> (as NO <sub>2</sub> )	18	1.7/2	14	22
HCN	about 0.2	4	0.05 (a)	2.5
TDI	-	0.7/0.9	-	-
NH <sub>3</sub>	about 0.2	(b)	traces	
amines	traces		(c)	n.a.
nitriles			traces	
N <sub>2</sub> O	-		traces	-

(a) locally much higher value (b) not available (c) not detected

Table 5 comparison of gas yields from various 1 m<sup>2</sup> pool fires

## ADVANCEMENT IN USE OF LAB-SCALE TESTS TO PREDICT REAL FIRE SCENARIOS FOR CHEMICALS

It is generally admitted that lab-scale fire tests suffer from apparatus dependancy, more than large scale tests, even for versatile tools like the Cone calorimeter (ISO 5660), or the 50kW flammability apparatus developed by Tewarson<sup>27</sup> and co-workers. However, they are worldwide recognised tools for ranking materials and more generally for assessing thermal as well as non thermal fire damage<sup>28</sup> regarding building products and polymers, as a result of tremendous efforts undertaken over the two last decades. Addressing the fire behaviour of chemicals is a relatively recent challenge for those equipments which are promoted for instance in Europe by laboratories such as VTT, ISSEP<sup>29</sup> (use of a cone calorimeter), and Rhône-Poulenc (use of a special version of the Tewarson apparatus<sup>30</sup>) in the framework of EU sponsored R&D like Mistral (MIH-STEP 92), Warehouse Fires (MIH-STEP96), or Combustion (STEP109)<sup>31</sup>.

	fire tests on diuron		fire tests on dimethoate		
	INERIS (large-scale) mg/g (b)	Rhône-Poulenc (Tewarson) mg/g	INERIS (large-scale) mg/g (b)	VTT CC (50 kW/m <sup>2</sup> ) mg/g	VTT CC (25 kW/m <sup>2</sup> ) mg/g
CO <sub>2</sub>	1136	843	(a)	(a)	(a)
CO	68	78	(a)	(a)	(a)
NO <sub>x</sub>	25	5	2	14	4.5
HCN	13	13	8	6.7	5.2
HCl	160	144			
SO <sub>2</sub>	-	-	175	560	510
CH <sub>3</sub> SH	-	-	88	not determined	not determined
soot	yes	yes	yes		
residue	yes	yes	yes	not reported	not reported

(a) not relevant, since lab-scale tests were performed with pure active chemicals, contrary to large-scale tests in the INERIS gallery. (b) referring to the pure active chemical

table 6 : comparison between large-scale and lab-scale tests on chemicals

All authors of this paper are involved in further work regarding how far so-called lab-scale tests may help large-scale techniques and modeling tools to give a better appraisal of the real fire behaviour of

chemicals. Table 6 summarises experimental data on two pesticides (diuron and dimethoate) for which some comparisons are possible, and seems to justify some optimism. It must be outlined, however, that accurate comparisons are difficult since fully commercial grades were used in large-scale tests, while pure active chemicals were burnt on the small scale (This background justifies in particular the absence of data regarding CO and CO<sub>2</sub> yields in the dimethoate large-scale test). Data regarding lab-scale from VTT<sup>32</sup> dealing with dimethoate and results reported by Rhône-Poulenc on diuron are relevant for basic comparisons with large-scale tests in well ventilated situations (21% of O<sub>2</sub> in fresh air stream in all combustion systems).

Similar comparisons dealing with other N-containing fuels mentioned previously would have led in the same way to more pessimism to date, especially with TDI<sup>23</sup>. When testing liquids is concerned, lab-scale procedures require special care and may still need improvements, as suggested by work in progress<sup>33</sup>.

## CONCLUSIONS

The large-scale experiments on chemicals carried out by INERIS which have been briefly overviewed in this paper have revealed how variable the fire behaviour of chemicals may be, depending notably on their chemical structures and physico-chemical properties. In terms of chemical fate in particular, we have shown how different the issue may be, depending on the product, the type of potentially hazardous chemical element involved and the size of the experiment.

An extended appropriate use of full-scale tests together with parametric studies on adequate lab-scale tests will still be needed in the future to improve understanding of scale effects and to provide via simple routes adequate knowledge of the behaviour on chemicals which are so numerous and often much more complex in their formulation than classical hydrocarbons.

In the light of experience achieved to date, we consider in most cases the following data as conservative values for risk assessment purposes related to fire behaviour of large storages of various industrial chemicals in well ventilated conditions :

- \*average burning rate : 20 to 60 g m<sup>-2</sup> s<sup>-1</sup> (sulfur storages would justify an exceptional lower burning rate assumption),
- \*N conversion rate into nitrogenated toxic compounds 40 % max (NO<sub>x</sub>, and HCN, isocyanates if relevant),
- \*S conversion rate into sulfur gaseous compounds : 100%,
- \*Cl conversion rate into chlorinated gases 100 % (most of the time 100 % into HCl)
- \*other halogens conversion rates into related halogenated acid : 100 %,
- \*survival fraction (in case of very toxic compound) : 1 to 2 %.

## ACKNOWLEDGEMENTS

The authors wish to thank public or private bodies which make the work possible by their financial support or their technical assistance, namely :

- the Commission of the European Community (supporting and promoting the Mistral I and II European projects)
- the International Isocyanate Institute Inc (fire behaviour of aromatic isocyanates)
- the French Ministry of the Environment (Industrial Environment Service).

## REFERENCE LIST

- 1 S.Cole, "A review of the Background and Direction of European Community Research in Major Industrial Hazards", paper presented at the SRA 4th conference "European Technology and Experience in safety analysis and Risk Management : ten years after the Seveso Directive", Rome, Italy, 18/19 October 1993.
- 2 R.Koivisto and D. Nielsen, "FIRE - a database on chemical warehouse fires", J. of Loss Prev. Process Ind., 1994, vol 7, n°3 pp 209-215
- 3 H. Wackerlig, "The aftermath of the Sandoz fire", Fire and prevention, n° 199, May 1987.
- 4 ISO TR 9122-4 "Toxicity testing of fire effluents- Part 4 : the fire model", 1993 (F)
- 5 K.A. Notarianni, D.D. Evans, W.D. Walton, D. Madrzykowski, J.R Lawson, and H. Koseki, "Smoke Production from large oil pool fires", Interflam'93. Proceedings of the 6th Int. Conference, Oxford (1993)
- 6 V. Blinov and G. Khudiakov (revised by H.C.Hottel), "Certain Laws Governing the Diffusive Burning of Liquids", Fire Research Abstract and Reviews, 1 p 41 (1958)
- 7 A.R. Hall, "Pool Burning", Oxidation and Combustion Reviews, 6 (1973) 169-225
- 8 H. Koseki, "Combustion Properties of Large Liquid Pool Fires", Fire Technology, August 1989
- 9 V. Babrauskas, "Estimating Large Pool Fire Burning Rates", Fire Technology (19) 1983.
- 10 M. Dahlberg, "The SP Industry Calorimeter, for rate of heat release measurements up to 10 MW, SP report 1992:43.
- 11 J.P. Pineau, C. Cwiklinski, G. Marlair, C. Michot, "Evaluation of products emitted during accidental fires in dangerous substances", paper presented at the ER'91 Conference, Calgary, Canada, 28/30 May 1991
- 12 G. Marlair, C. Cwiklinski, " Large-scale testing in the INERIS fire gallery : a Major Tool for both Assessment and Scaling-up of Industrial Fires", Proceedings of the 1st Industrial Fires CEC Workshop, Apeldoorn, The Netherlands, 11/12 march 1993, EUR 15340 EN.
- 13 R D. Peacock & V.Babrauskas, "Analysis of Large-scale Fire Test Data", Fire Safety Journal, 17, (1991) 387-414
- 13 bis T. Hirano and K. Saito, "Fire spread phenomena : The role of observation in experiment", progress in Energy and combustion sciences, vol 20, pp 461-485, 1994
- 14 R.I. Emori and K. Saito, "A study of Scaling Laws in Pool and Crib Fires", Combustion Science and Technology, 1983, vol 31, pp 217-231
- 15 E. Casale, G. Marlair, "Heptane Fire tests with Forced Ventilation", Proceedings of the International Conference on Fires in Tunnels, Boras, Sweden, October 10-11, 1994.
- 16 C. Cwiklinski, "Incendie dans les stockages de produits phytosanitaires. Les apports de l'essai en grand", (in French), Review RGS, 110, Jan-Febr. 1992, 41-45
- 17 G. Atkinson and S. F. Jagger, "Exposure of organophosphorus pesticides to turbulent diffusion flames", J. Loss Prev. Process Ind, 1992, vol 5, n°5
- 18 C. Cwiklinski, "L'essai en grand - Une approche préventive et prévisionnelle pour l'incendie en milieu industriel", (in French), review RGS, 97, Oct 1990.

- 19 D.S. Burgess, A. Strasser, J. Grumer, "Diffusive Burning of Liquid Fuels in Open Trays", Fire Research Abstract and Reviews, 3 (1961) pp 177/192
- 20 H. Bartelds, E. Smit, M. Molag, "Emissions from medium scale fires of chemicals", Industrial Fires workshop Proceedings, Apeldoorn, 11/12 March 1993, The Netherlands, EUR 15340 EN
- 21 A Hamins and al, "Heat Feedback to the Fuel Surface in Pool Fires", Combustion Science and Technology, 1994, vol 97, pp 37-62.
- 22 G. Marlair, F.H. Prager, H. Sand, "The Commercially Important Di-isocyanates in Fire Conditions. Part 2 : Polymeric 4,4' di-isocyanate diphenyl méthane (PMDI)", Fire and Materials, 1993
- 23 G. Marlair, F.H. Prager, H. Sand, "The Commercially Important Di-isocyanates in Fire Conditions. Part 1 : Toluene Di-isocyanate (TDI)", Fire and Materials, vol 17, 91-102 (1993)
- 24 G. Marlair, H. Sand, "Assessment of the Fire Hazard Presented by a Burning Pool of Toluene Diisocyanate (TDI), Cellular Polymers, vol 11, n°1, 1992
- 25 G. Weiss, Hazardous Chemicals Data Book, 2nd edition, ndc, USA, 1986..
- 26 R.L. Alpert and E.J. Ward, "Evaluation of Unsprinklered Fire Hazards", Fire safety Journal, 7 (1984) 127-143
- 27 A. Tewarson, "Heat release rate in fires", Fire and Materials, n°4 (1980) pp 185-194
- 28 A. Tewarson, "Nonthermal Fire Damage", Journal of Fire Sciences, vol 10 - May/June 1992
- 29 H. Breulet and S. Desmet, "Characterization of Industrial liquids by means of the Cone calorimeter", paper presented at the 2nd european workshop on Industrial Fires, Cadarache, France, May 1994.
- 30 C. Costa, Mistral 1 project, final report regarding the contribution of Rhône-Poulenc, ref. T/SE/SEC/352/94/372.
- 31 S. Cole and S. Wicks, Proceedings of the Industrial Fires Workshop held in Apeldoorn, The Netherland, March 1993, EUR 15430 EN
- 32 R. Kakko and al, "Toxic combustion products of three pesticides", J. Loss Prev. Process Ind., 1995, vol 8, n°2 pp 127-132.
- 33 S.Desmet (ISSEP), O.Milovanovic (Dow Europe S.A.), A.Tewarson (Factory Mutual), private communications (1995).